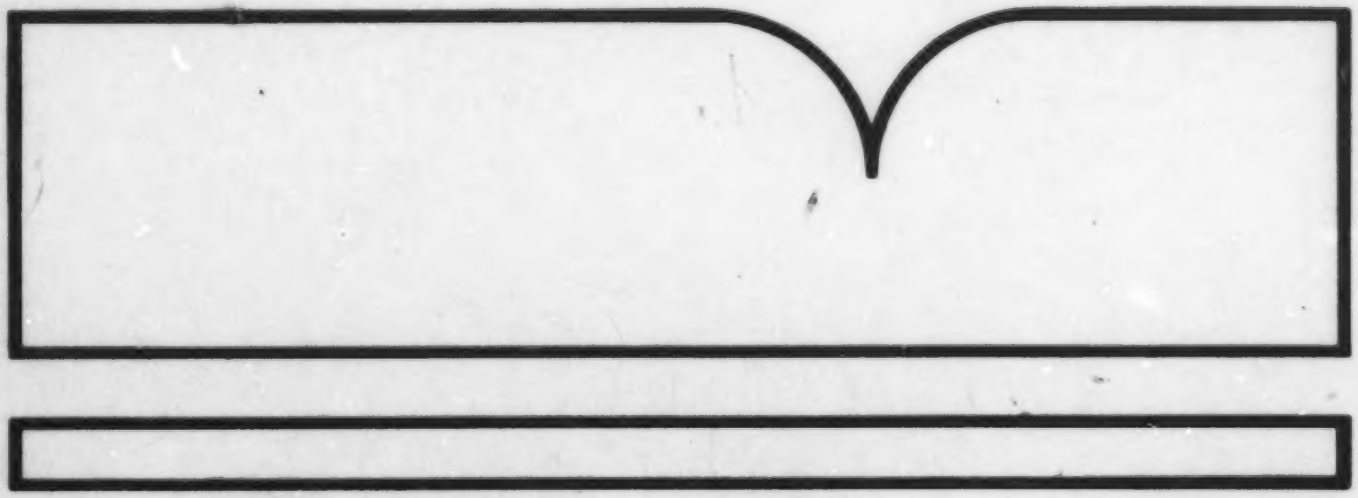
PB81-200800

Controlling Sulfur Oxides

(U.S.) Environmental Protection Agency
Washington, DC

Aug 80



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Office of Research and Development

EPA

Research Summary

Controlling Sulfur Oxides

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Coal is formed from the highly compressed remains of the abundant plant and animal life that existed some 200 to 250 million years ago. Thus it is not surprising that the five most abundant elements in coal—carbon, oxygen, hydrogen, sulfur, and nitrogen—are also five of the principal elements of life. Two of these elements—sulfur and nitrogen—present major combustion emission problems.

About 65 million metric tons of sulfur oxide pollutants are annually emitted into the atmosphere by the world's industrialized societies. The central and northeastern United States, southern Canada, and northern Europe account for three quarters of this total, but represent only one percent of the global surface area. The resulting concentration of sulfur oxides cause adverse human health effects, are a principal contribution to acid precipitation, and lead to significant reductions in visibility. Fortunately, over the past decade, the industrialized nations have made excellent progress in developing sulfur control technologies for new power plants.

This Research Summary describes EPA's program to develop new and improve existing technologies for sulfur oxides control. As we increasingly turn to coal as the primary utility and industrial fuel, while trying to deal with the problems of acid precipitation, visibility degradation, and unhealthy air, we will have to confront the fact that most of the sulfur oxides which will be emitted over the next two decades will come from plants existing today. If we vigorously pursue the successful demonstration of control technologies and then take advantage of them, especially those which can reduce emissions from existing plants, the adverse health and environmental effects of the troublesome sulfur oxides can be significantly reduced.

Stephen J. Gage
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for Research and Development

Cover Photo: EPA Documerica

BIBLIOGRAPHIC INFORMATION

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KEYWORDS: *Air pollution, *Sulfur oxides.

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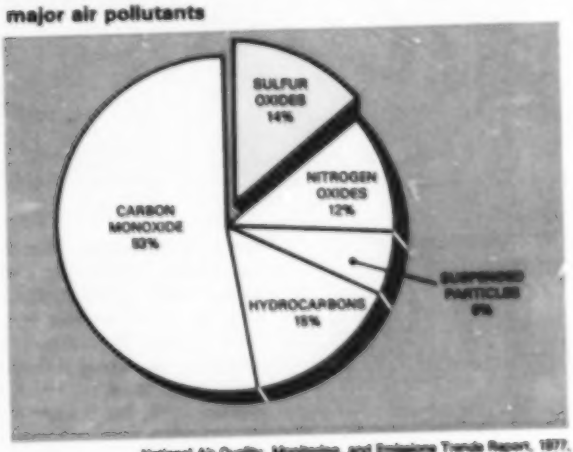
sulfur oxides problem

More than 25 million metric tons of sulfur oxides (SO_x) are emitted annually in the United States. This is about a quarter of the yearly total of sulfur oxides released from human activities and natural sources throughout the world.

Sulfur oxides account for approximately 14 percent of the total estimated national air pollutant emissions. Released primarily in the form of sulfur dioxide, they are converted by atmospheric processes to sulfates which interfere with normal breathing patterns, reduce visibility, and contribute to the formation of acid rain.

major air pollutants



National Air Quality, Monitoring, and Emissions Trends Report, 1977, EPA, December 1978.

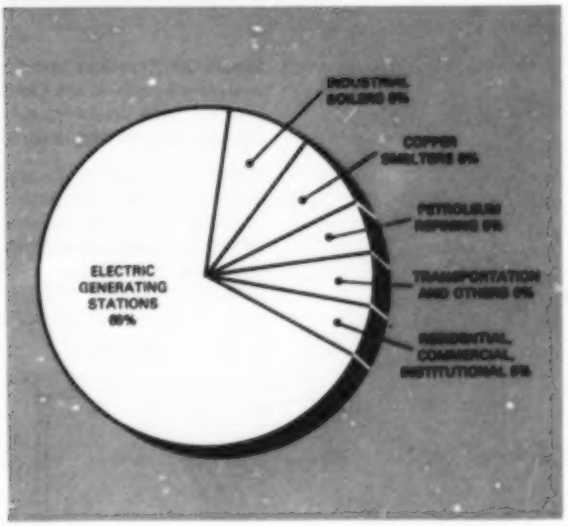
sources of SO_x

More than two thirds of all national sulfur oxide emissions result from fuel combustion in electric generating stations. An additional 8 percent of SO_x emissions result from fuel combustion in industrial boilers. Copper smelters are the largest noncombustion source of SO_x emissions, followed by petroleum refineries. Additional SO_x pollutants are released by furnaces used to heat homes, businesses, and public institutions. A small amount, less than 5 percent, is derived from the exhaust of cars, trucks, aircraft, and other vehicles.

The largest single source of SO_x is coal combustion. Sulfur is a natural contaminant of coal, and is almost completely

converted to sulfur oxide when coal is burned. In the United States during the 1950's and 1960's, many industries turned from coal to cleaner fuels such as oil and gas to avoid polluting the atmosphere. Now that supplies of oil and gas are becoming scarce, industries are compelled to use coal once again.

sulfur oxides emissions sources



EPA Environmental Outlook, 1980.

increased use of coal

Annual consumption of coal by the electric power utilities is expected to increase from 405 million metric tons per year in 1975 to between 600 million and 1 billion metric tons in 2000. As a result, the amount of SO_x generated by these utilities could increase from about 20 million to 41 million metric tons per year during the same period. If SO_x control systems are used, however, future emissions can be kept at approximately the current annual level.

About 95 percent of all sulfur oxides are in the form of sulfur dioxide (SO_2), a colorless gas that when cooled and liquified can be used as a bleach, disinfectant, refrigerant, or preservative. In the atmosphere, however, SO_2 is a precursor of highly destructive sulfates (SO_4), which are formed by the chemical addition of oxygen (O_2). SO_4 is not a stable compound, however, and in the presence of water (H_2O) it frequently forms sulfuric acid (H_2SO_4), a component of acid rain.

health effects

As the concentration of sulfur oxides in the air increases, breathing becomes more difficult, resulting in a choking effect known as pulmonary flow resistance. The degree of breathing difficulty is directly related to the amount of sulfur

compounds in the air. The young, the elderly, and individuals with chronic lung or heart disease, are most susceptible to the adverse effects of sulfur oxides.

Sulfates and sulfur acids are more toxic than sulfur dioxide gas. They interfere with normal functioning of the mucous membrane within the respiratory passages, increasing vulnerability to infection. The toxicity of these compounds varies according to the nature of the metals and other chemicals that combine with sulfur oxides in the atmosphere.

visibility

Small particles suspended in a humid atmosphere are the major cause of reduced visibility in the eastern United States. Over the past 25 years, visibility on an average summer day has decreased from 15 to 8 miles. Sulfates constitute 30 to 50 percent of the suspended particles.

acid rain

Acid rain is composed primarily of two acids: sulfuric (H_2SO_4) and nitric (HNO_3). Sulfuric acid, resulting from sulfur oxide emissions, comprises from 40 to 60 percent of acid rain depending on regional emission patterns. Acid rain is a major problem throughout the world, especially in Scandanavia, Canada, and the eastern United States.

Rain in the northeastern United States averages 10 to 100 times the acidity of normal rainwater. More than 90 lakes in the Adirondack Mountains of New York State no longer contain fish because the increased acidity of lake water has caused toxic metals in the lake beds and surrounding soils to be released into the lakes. Similar effects are beginning to occur in other areas of the United States such as northern Minnesota and Wisconsin.

Preliminary studies indicate that the direct effects of acids on foliage and the indirect effects resulting from the leaching of minerals from the soil can reduce the yield from some agricultural crops.

materials deterioration

Sulfur acids corrode materials normally considered to be durable, such as metals, limestone, marble, mortar, and roofing slate. As a result, acidic sulfates are destroying statuary and other archeological treasures that have resisted deterioration for thousands of years. These include such well-known structures as the Parthenon in Greece and the Taj Mahal in India, as well as lesser known bronze and stone statuary in U.S. cities.

Corrosive destruction of statuary is most severe in areas where droplets of moisture collect. Sulfates and other atmospheric particles form a crust on the statuary that retains moisture and promotes the formation of sulfuric acid. This acid destroys the surface of the statuary, causing smooth metal sculptures to become pitted, and resulting in such severe spalling of stone figures that the outlines of the features become blurred.

Center for Archaeometry, Washington University

SO_x emissions standards

In accordance with the 1977 Clean Air Act Amendments, the EPA has established regulations that require electric power companies and industries to take steps to reduce SO_x emissions.

National Ambient Air Quality standards for sulfur oxides establish a maximum safe level of the pollutant in the atmosphere. According to these standards, atmospheric concentrations of SO_x should not exceed 0.5 parts per million (ppm) during a 3-hour period, or 0.14 ppm during a 24-hour period. The annual mean concentration should not exceed 0.03 ppm.

In addition, EPA requires most new fossil-fuel fired steam generators to meet its SO_x New Source Performance Standards. These standards apply to all boilers built after August 1971 that are capable of producing more than 250 million British Thermal Units (Btu) of heat per hour. The standards limit emissions from both industrial and electric utility boilers to no more than 0.8 pounds of SO_2 per million Btu of heat input, if oil is burned. If coal or a coal-derived fuel is burned, emissions must not exceed 1.2 pounds of SO_2 per million Btu. Utility boilers built after September 1978 have an additional requirement to install some form of SO_x control equipment to achieve a reduction in potential SO_2 emissions. For

coal-fired units, the required level of reduction varies from 70 percent for low-sulfur coals to 90 percent for high-sulfur coals. Oil-fired utility units are required to achieve a 90 percent reduction in potential SO_2 emissions.

The most prevalent means of SO_x control are the flue gas desulfurization (FGD) systems, which remove sulfur dioxide from exhaust gases before they are emitted into the air. Numerous public and private organizations are conducting research to both improve existing control technologies and develop new ones.

EPA's research program

EPA's Office of Research and Development (ORD) is developing improved technologies for sulfur oxides control in four major areas:

- fuel cleaning
- flue gas desulfurization
- combustion of coal-limestone mixtures
- coal liquefaction and gasification.

Research is being performed by EPA laboratories and various public and private institutions. The Office of Research and Development provides assistance in conducting research and demonstration projects through grants, contracts, and cooperative agreements.

fuel cleaning

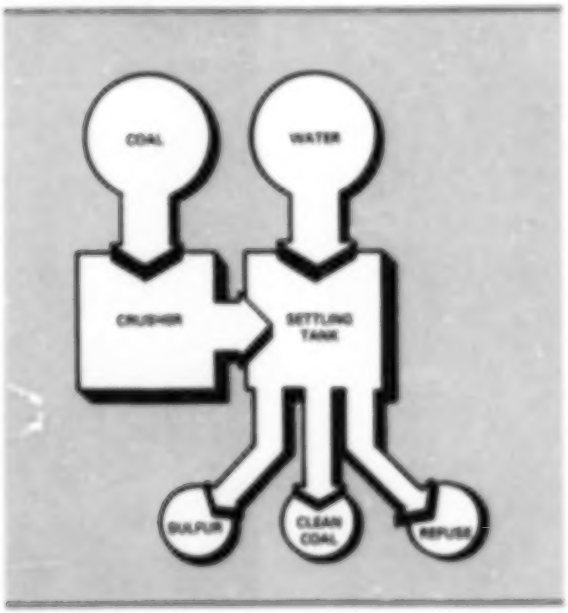
coal cleaning

About 450 to 500 coal cleaning plants are operating in the U.S. Fifty percent of all domestically consumed coal is mechanically cleaned to remove dirt and other impurities. Some coal used for refining metals is cleaned to remove sulfur, but coal destined to be burned to generate steam for power plants and industries is usually not processed to remove sulfur.

Coal contains sulfur in two forms: mineral sulfur, in the form of pyrite, and organic sulfur that is chemically bound in the coal. Most mineral sulfur can be removed by mechanical coal cleaning processes, but removing organic sulfur requires chemical processing.

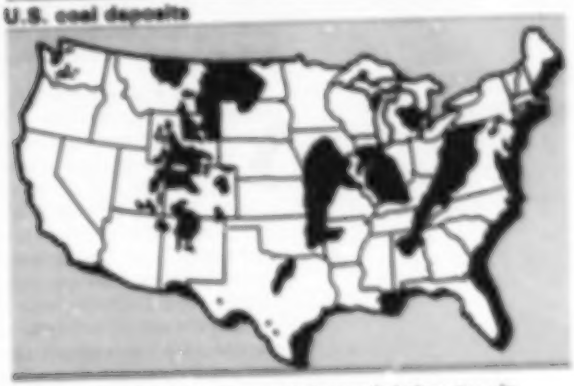
physical cleaning

To remove mineral sulfur, the coal is crushed, washed, and then separated from impurities during a settling process. From 40 to 90 percent of the total sulfur content in coal can be removed by this physical cleaning process. Cleaning effectiveness depends on the size of pyritic sulfur particles and the proportion of sulfur in pyritic form.



Nearly half of the sulfur in coals from eastern Kentucky, Tennessee, Georgia, and Alabama, and most of the sulfur in coal from the western mountain states is in the pyritic form and is relatively easy to remove by mechanical cleaning. The combination of physical coal cleaning and partial flue gas desulfurization enables many generating stations to meet SO_x emission standards at less expense than using flue gas desulfurization alone.

U.S. coal deposits

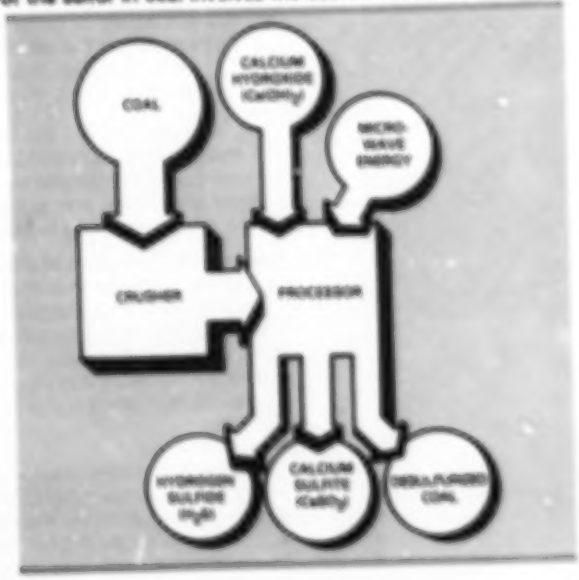


chemical cleaning

ORD's Industrial Environmental Research Laboratory in Research Triangle Park, North Carolina (IERL-RTP) is involved in a program to advance two important chemical coal cleaning technologies: microwave desulfurization and hydrothermal desulfurization.

microwave desulfurization

One innovative technique for removing as much as 70 percent of the sulfur in coal involves the use of microwave energy.



The coal is crushed, then heated for 30 to 60 seconds by exposure to microwaves. Mineral sulfur selectively absorbs this energy and escapes from the coal in the form of hydrogen sulfide gas (H_2S). Adding calcium hydroxide ($Ca(OH)_2$) to the crushed coal causes the organic sulfur in the coal to convert to calcium sulfite ($CaSO_3$) when it is exposed to the microwave energy.

The coal is then washed with water to remove the calcium sulfite and other impurities. The hydrogen sulfide gas (H_2S) resulting from microwave desulfurization can be collected and processed to recover marketable elemental sulfur (S).

hydrothermal desulfurization

Hydrothermal desulfurization, developed by Battelle Laboratories in Columbus, Ohio, is undergoing further refinement through experiments sponsored by the Office of Research and Development. In this process, the coal is crushed to a fine particle size and mixed with a solution of sodium and calcium hydroxides (NaOH and $Ca(OH)_2$). When this mixture is heated to 275° C under pressure, nearly all of the inorganic sulfur and 20 to 50 percent of the organic sulfur is converted to sodium and calcium sulfites (Na_2SO_3 and $CaSO_3$). The hydrothermally treated coal is then rinsed to remove the converted sulfur compounds, and the liquid derived from the washing can be processed to recycle the sodium and calcium hydroxides.

Although research remains in the experimental stages, hydrothermal desulfurization appears to be an effective means of removing sulfur from coal. ORD is directing current efforts towards reducing the high cost of this process by developing alternative methods of drying the coal and recovering the sodium and calcium hydroxides.

vehicular fuel cleaning

Gasoline, diesel fuel, and jet fuel all contain sulfur which is emitted in the form of sulfur oxides after combustion. Although motor vehicle emissions currently account for only about 3 percent of total national sulfur oxide emissions, EPA is concerned about them for two reasons.

First, the catalytic converter being installed in cars to control hydrocarbon and carbon monoxide emissions can convert exhaust sulfur dioxide to the more toxic compound, sulfuric acid. These acid fumes could adversely affect the health of people driving in heavy traffic.

Second, the production of diesel-powered vehicles is expected to increase; diesel engines may be installed in 25 percent of all new cars by 1985. Because diesel fuel is high in sulfur content, its combustion results in emissions of large amounts of sulfur dioxide and sulfuric acid. EPA is investigating the feasibility and cost of reducing the sulfur content of diesel fuel from its current average of 2,000 ppm to 200 ppm.

Gasolines vary widely in sulfur content; gasoline produced in the Northeast has roughly two times the sulfur content of gasoline produced in the Pacific Northwest. Regional differences are due to the type of crude oil processed, variations in refinery processes, and the grades of gasoline produced.

For example, unleaded and premium grade gasolines contain less sulfur content than regular grade. EPA is examining the possibility of reducing the sulfur content of all grades of gasoline from the current range of 350-400 ppm to 100 ppm.

Commercial jet fuels used in the U.S. have an average sulfur content of about 600 ppm. Some jet fuels contain up to 2,000 ppm sulfur, and airline specifications allow a maximum of 3,000 ppm. Researchers believe that the sulfur content of jet fuel can be reduced to 200 ppm.

Sulfur can be removed from diesel fuel, gasoline, and jet fuels during the refining process. When the sulfur in petroleum is exposed to hydrogen in the presence of a catalyst, hydrogen sulfide gas is formed. This compound can be commercially marketed.

potential reduction of sulfur in fuels by 1990

	current sulfur content (ppm)	potential sulfur content (ppm)	cost per gallon (cents)
gasoline	350-400	100	1.9
diesel fuel	2000	200	3.4
jet fuel	600-3000	200	2.5

Researchers at ORD's Environmental Sciences Research Laboratory in Research Triangle Park, North Carolina have been studying the costs and benefits of reducing the sulfur content of vehicular fuel. They have found that added costs for desulfurizing gasoline to meet a 100 ppm standard by 1990 would average 1.9 cents per gallon. Reducing the sulfur content to 200 ppm would cost 3.4 cents per gallon for diesel fuel, and 2.5 cents per gallon for jet fuel. Further research is needed to develop more economical methods of removing sulfur from vehicular fuels.

flue gas desulfurization

Flue gas desulfurization (FGD) is the most commonly used method of removing sulfur oxides resulting from the combustion of fossil fuels. It is also the method that is best suited to control SO_x emissions from copper smelters. FGD processes result in SO_x removal by inducing exhaust gases to react with a chemical absorbent as they move through a long vertical or horizontal chamber. The absorbent is dissolved or suspended in water, forming a solution or slurry that can be sprayed or otherwise forced into contact with the escaping gases. The chamber is known as a scrubber, and the process is often referred to as wet scrubbing.

More than 50 different flue gas desulfurization processes have been developed, but only a few have received widespread use. Of the systems currently in operation, 90 percent use lime or limestone as the chemical absorbent.

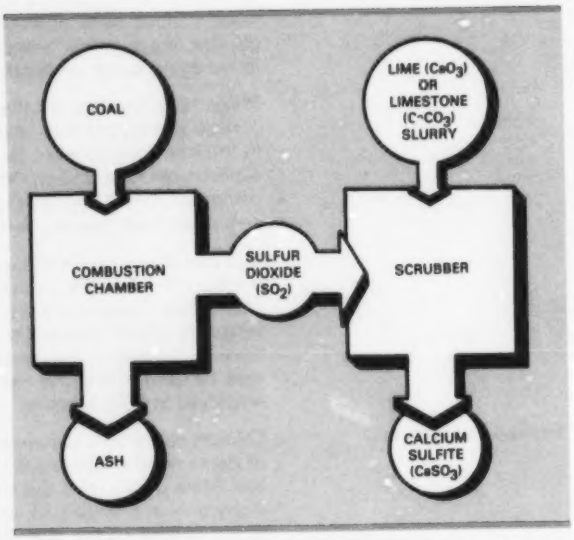
In a lime slurry system, the sulfur dioxide reacts with lime to form calcium sulfite and water.

$$\underset{\text{sulfur dioxide}}{SO_x} + \underset{\text{lime}}{CaO} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{calcium sulfite}}{CaSO_3} + \underset{\text{water}}{H_2O}$$

The use of limestone results in a similar reaction, but also yields carbon dioxide.

$$\underset{\text{sulfur dioxide}}{SO_2} + \underset{\text{limestone}}{CaCO_3} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{calcium sulfite}}{CaSO_3} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

A few problems have arisen in the operation of the lime and limestone FGD systems, and EPA's Industrial Environmental Research Laboratory in Research Triangle Park, North Carolina, has been successful in developing solutions. Current efforts are directed towards using the limestone more efficiently, removing more SO_2 from the exhaust gases, improving equipment reliability, and altering the composition of the waste sludge so that it can be more easily disposed of in landfills.



adipic acid additive

The recent discovery that the addition of adipic acid to FGD limestone can increase the level of SO_2 removal from 85 percent to 95-97 percent represented a major breakthrough in SO_2 removal technology. Adipic acid, a crystalline powder derived from petroleum, is available in large quantities.

EPA experiments have shown that when a limestone slurry reacts with SO_2 in the scrubber, the slurry becomes very acidic. This acidity limits SO_2 absorption. Adding adipic acid to the slurry slightly increases the slurry's initial acidity, but prevents it from becoming highly acidic during the absorption of SO_2. The net result is an improvement in scrubbing efficiency.

Researchers have shown that adipic acid can reduce total limestone consumption by as much as 15 percent. Furthermore, the additive is nontoxic (it is used as a food additive), and does not degrade calcium sulfite sludge ($CaSO_3$) and gypsum ($CaSO_4$), the FGD wastes.

Adipic acid is not currently being used in commercial FGD systems. Full scale tests at an operating electrical generating station are in the planning stage.

limestone utilization

Adding adipic acid is one way to increase limestone utilization in the scrubber system. Researchers are studying other factors that affect SO_2 absorption and limestone utilization, including the limestone's particle size, impurities, and geological structure.

Limestone used in a scrubber system is crushed into small particles to allow more calcium carbonate ($CaCO_3$) molecules on the surface of the particles to react with the sulfur dioxide (SO_2) gas. ORD scientists are testing two sizes of limestone particles: a coarse grind, similar to that of sugar or salt; and a fine grind, similar in consistency to

flour. Various types of limestone, crushed to the same particle size, are currently being compared for their effectiveness in removing sulfur oxides from exhaust gases.

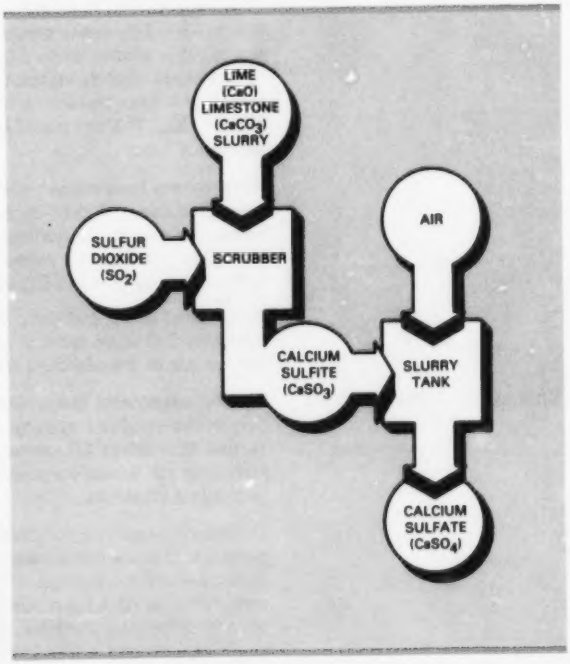
These tests have shown that different limestones of equal particle size vary in their absorption effectiveness. Impurities in the limestone account for part of this difference. Recent experiments have shown that the presence of magnesium carbonate, the main impurity in limestone, inhibits calcium carbonate from reacting with the sulfur dioxide.

The presence of such impurities, however, cannot fully account for variations in the efficiencies of various limestones. Researchers are investigating such geological factors as crystal size and pore size to determine why some kinds of limestone work better than others. These data can then be used to improve the utilization of all limestones employed in FGD systems.

forced oxidation

Calcium sulfite that is formed during the scrubbing process presents another important problem. This substance settles and filters poorly, and can be removed from the scrubber slurry only in a semiliquid, or paste-like, form which must be stored in lined ponds. IERL-RTP is developing a way to solve this problem through a process called forced oxidation.

Forced oxidation requires air to be blown into the tank that holds the used scrubber slurry, composed primarily of calcium sulfite and water. The air oxidizes the calcium sulfite to calcium sulfate.



$$CaSO_3 + H_2O + 1/2\,O_2 \longrightarrow CaSO_4 + H_2O$$

calcium sulfite + water + Oxygen → calcium sulfate + water

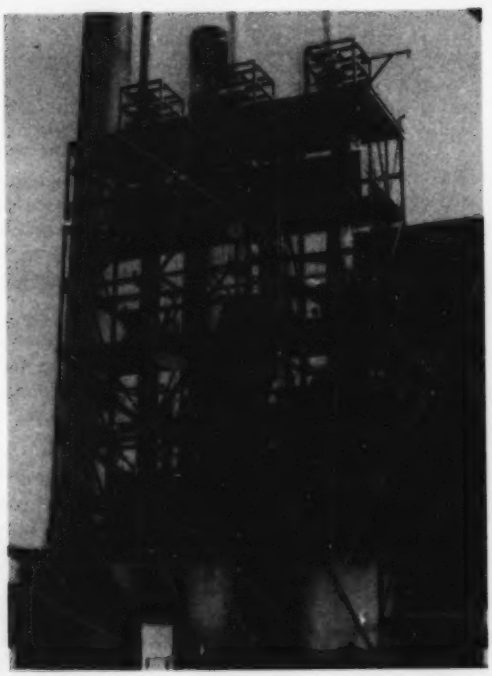
The calcium sulfate formed by this reaction grows to a larger crystal size than does calcium sulfite. As a result, the calcium sulfate can easily be filtered to a much drier and more stable material which can be disposed of as landfill. In some areas, the material may be useful for cement or wallboard manufacture or as a fertilizer additive.

Another problem associated with limestone scrubbers is the clogging of equipment due to calcium sulfate scale. Forced oxidation can help control scale by removing calcium sulfite from the slurry and by providing an abundance of pure gypsum (calcium sulfate) to rapidly dissipate the supersaturation normally present. The process also requires less fresh water, which is scarce in many western locations, for scrubber operation.

Current experiments at Research Triangle Park are directed toward testing various forced oxidation designs to find the best oxidation system using the least energy.

shawnee test facility

Since early 1972, EPA's Industrial Environmental Research Laboratory, Research Triangle Park, has been conducting



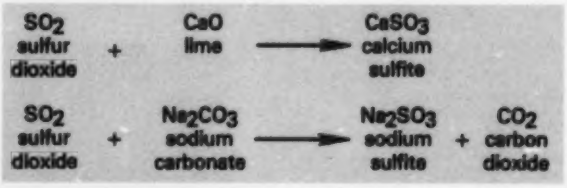
flue gas desulfurization tests at the Shawnee Lime and Limestone Wet Scrubbing Test Facility near Paducah, Kentucky. This test facility uses the Shawnee Power Station, a coal-fired plant owned and operated by the Tennessee Valley Authority (TVA).

The facility, shown in the photo on the previous page, was built with three different FGD scrubber systems. Each system treats part of the exhaust gases from the generating station. Emissions from the facility are monitored and scrubber equipment is modified to find ways of solving operating problems and reducing costs. Recent tests are focusing on different methods of forced oxidation of lime and limestone slurries. Researchers are also examining the effectiveness of various slurry additives for increasing the efficiency of SO_2 removal systems.

Results of tests at the Shawnee prototype FGD facility are presented to commercial utility operators and FGD system manufacturers through workshops, conferences, and EPA publications.

dry scrubbing

Dry scrubbing is a modification of wet scrubbing flue gas desulfurization technology. As in other FGD systems, the exhaust gases combine with a fine slurry mist of lime or sodium carbonate. This system, however, takes advantage of the heat of the exhaust gases to dry the reacted slurry into particles of calcium sulfite and sodium sulfite.


SO2 sulfur dioxide + CaO lime → CaSO3 calcium sulfite
SO2 sulfur dioxide + Na2CO3 sodium carbonate → Na2SO3 sodium sulfite + CO2 carbon dioxide

The particles generated by this dry scrubbing process are then collected along with other particles from coal combustion in a baghouse collector. This collector uses fabric bags that function similar to those in a vacuum cleaner, which collect particles while permitting cleaned gases to escape.

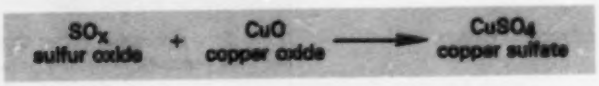
Dry scrubbing typically removes 70 percent of the sulfur dioxide in a waste gas stream. It is 15 to 30 percent cheaper to install and operate than a conventional wet scrubbing system. However, because dry scrubbing is less efficient than wet scrubbing, the technology has been limited to use with low sulfur coal.

Plans for future research include evaluating the performance and reliability of a full scale utility boiler equipped with a spray-dryer SO_2 control system. Improvements could make these dry scrubbing systems acceptable for general use by the late 1980's.

copper oxide adsorption

An experimental method of removing 90 percent of both sulfur and nitrogen oxides is being developed by IERL-RTP. In this process, combustion exhaust gases are moved over a

bed of copper oxide. Sulfur oxides combine with the copper oxide, forming copper sulfate.



Periodically, the copper oxide is regenerated with diluted hydrogen to produce a gas containing concentrated amounts of sulfur dioxide. Two or more copper oxide reactors are used to achieve continuous desulfurization.

The copper sulfate formed by this reaction serves as a catalyst, causing ammonia injected into the system to react with nitrogen oxides (NO_x) forming nitrogen gas and water. Researchers are conducting experiments to determine the optimum method of removing both sulfur and nitrogen oxides under various operating conditions. ORD is sponsoring the demonstration of copper oxide absorption technology at Tampa Electric Company's Big Ben Station near North Ruskin, Florida. It is expected that copper oxide absorption technology will soon be applicable to large coal-fired electrical generating stations.

smelter scrubbers

Copper ore contains large amounts of sulfur that are converted to sulfur oxides when the ore is processed. About two tons of sulfur dioxide (SO_2) are generated for each ton of copper produced.

Smelters produce two streams of gases containing sulfur oxides, a strong stream containing a 4 percent or greater concentration of SO_x, and a weak stream normally with less than a 2 percent concentration of SO_x. The strong stream is usually treated by a chemical process that converts SO_2 to sulfuric acid (H_2SO_4). In this process, SO_2 is cleaned and converted to SO_3. Then the SO_3 reacts with water, producing H_2SO_4. Thirteen of the sixteen copper smelters in the United States operate sulfuric acid plants. The sulfuric acid can be used in ore processing operations or sold to other industries.

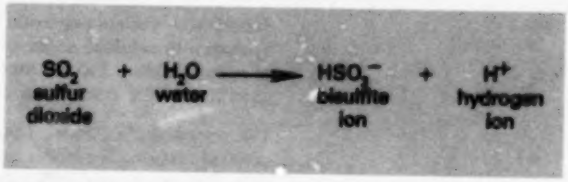
Most of the SO_2 emissions from copper smelters come from reverberatory furnaces. Eleven of the sixteen copper smelters operating in the United States use this type of furnace which burns gas, oil, or coal. When copper is heated, sulfur is released and mixes with gases from the burning fuel and with large quantities of air and is converted to SO_2. The concentration of SO_2 ranges from 0.5 to 3.5 percent, but rarely exceeds 2.5 percent. This level of SO_2 concentration is lower than the 4 percent or more required to process SO_2 into sulfuric acid (H_2SO_4), so the furnace exhaust gases are vented to the atmosphere. None of the reverberatory furnaces operating in this country are equipped with controls for SO_2 emissions.

A project is underway at the Industrial Environmental Research Laboratory in Cincinnati, Ohio, to identify SO_x emission control systems that are appropriate for use with copper smelters. Two of the most promising systems are

the citrate and magnesium oxide processes. Both processes concentrate SO_2 gas from the smelter furnace to allow the production of sulfuric acid.

citrate process

In the citrate process, sulfur dioxide is dissolved in water and thus removed from the exhaust system.



Adding citrate to the water increases the amount of SO_2 that the water will absorb because the citrate ion (CIT) chemically bonds with the hydrogen ions (H^+). Sulfur can then be removed from the citrate solution in the form of an SO_2 stream strong enough to be used in the acid plant and converted to marketable sulfuric acid.

magnesium oxide process

In the second SO_x control process, magnesium oxide is mixed with water to form a slurry. Washing the smelter gases with this slurry causes the SO_2 in the gases to combine with the magnesium and form magnesium sulfite.

The magnesium sulfite is collected, dried, and heated to temperatures of from 670° to 1000° C (1250° to 1800° F). The heat causes the magnesium sulfite molecules to break apart, regenerating magnesium oxide that can be used again, and a highly concentrated SO_2 gas that can be converted to sulfuric acid.

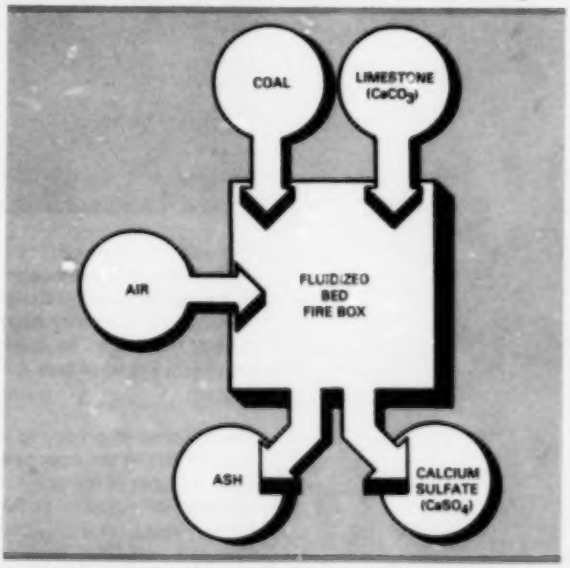
Both the citrate and the magnesium oxide processes are being tested for their effectiveness in removing SO_2 from the exhaust gases of industrial boilers and electric generating plants. The citrate process is being demonstrated in a copper smelter in Sweden and in a zinc smelter in Pennsylvania. The magnesium oxide process has been demonstrated in a smelter in Japan. The demonstrations have shown these processes to be at least 90 percent effective in removing SO_2 from exhaust systems. Adapting them to the U.S. smelting industry would be a major step in reducing national sulfur oxide emissions.

coal-limestone combustion

Since sulfur oxides are emitted from the stacks of electrical generating stations and industries, the initial approach to SO_x control concentrated on treatment of the waste gases in the stack. Recently, however, scientists and engineers at the IERL-RTP have been working with the U.S. Department of Energy and the electrical power industry to develop methods of removing sulfur oxides in the combustion area. Two promising burning techniques are currently receiving attention: fluidized bed combustion and the use of limestone coal pellets as fuel.

fluidized bed combustion

In the fluidized bed combustion process, a grid supporting a bed of crushed limestone or dolomite is set in the firebox. Air forced upward through the grid creates turbulence, causing the bed of limestone or dolomite to become suspended and move in a fluid-like motion. Natural gas is injected into the firebox and ignited, then pulverized coal is pushed into the combustion area and burned. Once the coal has started to burn well, the natural gas is shut off, and the fire is maintained by burning coal. Sulfur oxidized during



combustion reacts with the limestone or dolomite in the firebox forming calcium sulfate. Calcium sulfate and residual

limestone or dolomite from fluidized bed combustion can be disposed of in landfills or used in construction materials.

Fluidized bed combustion eliminates the need for flue gas desulfurization since the bed of limestone or dolomite can remove more than 90 percent of the sulfur oxides created during combustion. Furthermore, it is expected that fluidized bed combustion systems will cost less than conventional boilers with flue gas desulfurization systems.

Demonstrations of fluidized bed combustion technology are being conducted at several sites, including one at Rivesville, West Virginia. This technology is expected to be available for commercial application in the early 1990's.

limestone coal pellets

Burning pellets composed of a limestone and coal mixture is another way of eliminating the need for flue gas desulfurization. ORD research has shown that the combustion of these pellets in conventional stoker boilers not only reduces sulfur oxide emissions, but also enhances boiler performance.

The pellets are made by pulverizing coal and limestone and adding a binder material to form small cylinders. As the pellet burns, the calcium in the limestone absorbs the SO_2 generated from burning the coal, resulting in the formation of calcium sulfate ($CaSO_4$).

Ken Altshuler

The ability of the pellet to control sulfur emissions depends on the ratio of limestone to coal, pellet size, binder material, and types of coal and limestone used. For example, ORD has developed a binder material that enables as much as 87 percent of the SO_2 to be absorbed by the limestone when a pellet composed of two-thirds coal and one-third limestone is used.

The expense of preparing fuel with pellets would add about $15 per ton to the cost of coal, which is substantially less than the cost of installing and operating wet scrubber systems for industrial boilers. In the future, fuel pellets will be developed for a greater range of coal and boiler types. This research could enable users of high sulfur coal from eastern U.S. mines to meet SO_x pollution control requirements.

coal liquefaction and gasification

The Industrial Environmental Research Laboratory in Research Triangle Park is engaged in a program to develop and evaluate techniques of controlling pollution from coal liquefaction and gasification processes. Synthetic gas derived from coal will be commercially available by about 1985 to 1990. Liquid fuels from coal are expected to be available in the 1990's.

These fuels are not only far more useful than coal, but are also cleaner to burn. With the impetus of the 1973 oil embargo, consequent increases in the price of imported oil, and our abundant U.S. coal resources, the synthetic fuel industry may grow rapidly in the years ahead. The production of synthetic gas and oil is expected to consume 120 million tons of coal by 1990 and 300 million tons by 2000.

While prime responsibility for developing synthetic fuel processes lies with the Department of Energy, the Environmental Protection Agency must ensure that these processes do not create adverse health and ecological effects.

coal gasification

A very elementary process of coal gasification was designed in the late 1700's to fuel the gas lights that illuminated cities. Since that time, approximately 70 different coal gasification processes have been used commercially or are currently under development.

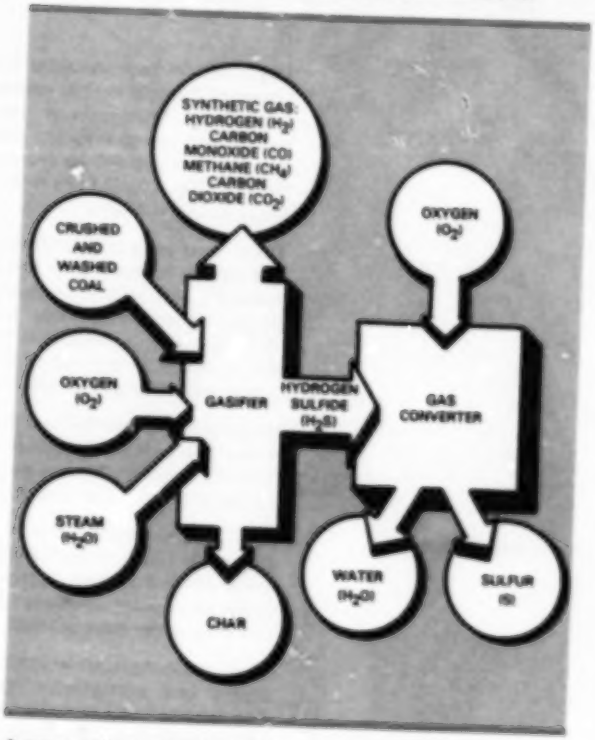
Three basic steps are common to all coal gasification processes: coal pretreatment, gasification, and gas cleaning. Coal pretreatment includes various stages of coal washing and pulverization. Gasification produces either a low- or high-heat content gas by applying heat and pressure, or using a catalyst to break down the components of coal. Coal is gasified in an atmosphere of limited oxygen. Generally, oxidation of the coal provides a gas containing carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), water (H_2O), methane (CH_4), and contaminants such as hydrogen sulfide (H_2S), and char.

Synthetic gas is composed primarily of carbon monoxide and hydrogen. Variations in the process may increase the quantity of methane formed, producing a gas that releases more heat when it is burned.

The sulfur in coal is converted primarily to hydrogen sulfide (H_2S) during the gasification process. It exits from the gasifier with the methane and synthetic gas, and is subsequently removed during the gas cleaning process. After

removal, the hydrogen sulfide is then converted to elemental sulfur (S) through partial oxidation and catalytic conversion.

An estimated 900 tons of sulfur flow daily through a plant using high sulfur Eastern coals. Thus, the collection, conversion, and removal of gaseous sulfur compounds is essential to prevent health and environmental damage. After the sulfur compounds have been removed, the synthetic gas can be burned without releasing dangerous emissions.



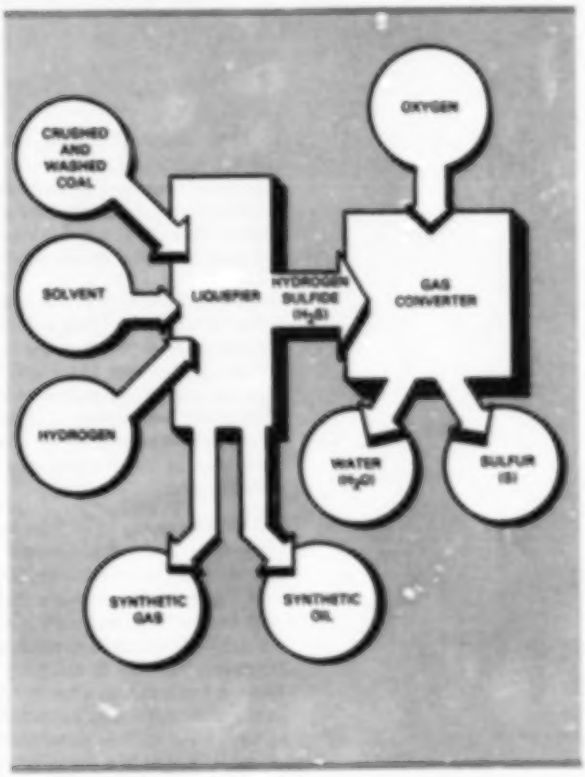
coal liquefaction

A process for converting carbon monoxide to liquid hydrocarbons was developed by Fischer and Tropsch in Europe in the 1930's, and tests and demonstrations of processes for producing synthetic oil from coal were initiated in the U.S. in the early 1960's.

There are two basic approaches in converting coal to oil. One involves using a gasifier to convert coal to carbon monoxide, hydrogen, and methane; followed by a condensation process that converts the gases to oils. The second approach involves using a solvent or slurry to liquefy pulverized coal and processing this liquid into a fuel similar to heavy oil. Solvents and slurries used in these processes are usually produced from the coal and recycled in the system. Recently developed liquefaction processes have combined the use of solvents and distillation techniques to produce hydrocarbon gas and various hydrocarbon liquids.

Processes involving solvents and slurries commonly remove sulfur from the liquified coal by using hydrogen (H_2) to convert the sulfur to hydrogen sulfide gas.

As in the gasification processes, this hydrogen sulfide is then partially oxidized to form elemental sulfur and water.



More than 85 percent of the sulfur in coal is removed during the liquefaction process. EPA research efforts currently focus on determining the sulfur content in synthetic oils produced by different liquefaction processes, and identifying ways to improve their sulfur removal efficiencies. EPA is also initiating programs to develop improved systems for preventing the escape of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) from the gas converter into the atmosphere.

costs of SO_x control

By 1990, electrical utilities will have invested between $10 and $20 billion for the construction and operation of flue gas desulfurization systems. The Office of Environmental Engineering and Technology at EPA Headquarters in Washington, D.C. has initiated several efforts to reduce the costs of sulfur oxide control technology.

One of these efforts involves searching for new methods of sulfur oxide control that will cost less than the wet scrubbing systems currently available. EPA is sponsoring workshop sessions with members of the electric utility industry and other groups to keep them informed of new cost-saving technological improvements of available systems, and to encourage their cooperation in building and operating test facilities to demonstrate new SO_x control technologies.

EPA is also trying to reduce costs by developing commercial markets for the waste products of sulfur oxide removal processes. Such products include gypsum, sulfur, and sulfuric acid. Gypsum is a valuable commodity used in making wallboard and other building materials, and sulfur and sulfuric acid are used extensively in the chemical industry. However, the cost of shipping these waste products to existing markets has often made them too expensive to be competitive with local resources. EPA is investigating the potential use of SO_x control waste products in the fertilizer industry. Sulfur is a plant nutrient, and since fertilizer is made locally in a large number of areas, shipping costs should not be a major deterrent to the use of the sulfur wastes. Developing other markets for these products will both reduce the net costs associated with SO_x removal and alleviate some of the problems associated with the disposal of wastes generated from SO_x control systems.

individual research projects

Selected research projects underway by or through the various ORD laboratories or offices are listed below.

industrial environmental research laboratory research triangle park, north carolina

- Sulfur Dioxide Oxidation in Scrubber Systems
- Miniplant Studies in Support of Fluidized-Bed Combustion Program
- EPA Shawnee Alkali Scrubbing Test Facility—Advanced Testing and Support Studies for Transfer of Technology to Full-Scale Operating Plants
- Investigation of NO_x, Nitrate, and Sulfate Formation in Laboratory Flames
- Emissions Assessment of Conventional Combustion Systems
- Coal Cleaning Technology Evaluation and Development
- Pilot-Scale Evaluation of Simultaneous NO_x/SO_x Flue Gas Treatment Technology
- Develop Comparative Economics of SO_x Control Processes
- Marketing of By-Products from SO_x Control Processes

industrial environmental research laboratory cincinnati, ohio

- Feasibility of Smelter Weak SO_2 Stream Control
- Evaluation of Baghouse and Optional FGD Demonstration on Smelter Weak SO_2

environmental sciences research laboratory research triangle park, north carolina

- Mesoscale Sulfur Balance Studies
- Sulfur Budget in Large Plumes
- Kinetic Study of Simulated SO_2, NO_x, Reactive Hydrocarbon-Polluted Atmospheres
- Continuous Monitoring of Particulate Sulfur Compounds by Flame Photometry
- Remote Atmospheric Measurement of SO_2 and CH_4 Using a $LiNbO_3$ Tunable Laser Source
- SO_2 and SO_4 Measurement Methods Evaluation
- Measurement of SO_2, SO_3, and H_2SO_4 from Fossil-Fueled Combustion Sources
- Measurement of H_2SO_4 Emissions from Selected Sources
- Develop and Evaluate Monitors for Detection of Sulfur Containing Gaseous Compounds
- Outdoor Smog Chamber Studies of Sulfur Emissions from Fuel Conversion Facilities
- Determination of SO_2 Mass Emission Rates by Remote Sensing
- Characterization of Primary Sulfate Emissions from Industrial/Residential Sources

- Cost of Sulfur Reduction in Mobile-Source Fuels to the Petroleum Refining Industry
- Sulfur Dioxide and Sulfates Material Damage Study—Part 4: Distribution in Cities
- Atmospheric Transport and Transformation from Coal-Fired Power Plants

office of environmental engineering and technology
washington, d.c.

- A Study to Support the Development of New Source Performance Standards for Control of SO_2, NO_X, and Particulates from Combustion Boilers
- Deposition, Retention and Dosimetry of Inhaled Reaction Products Which May Result from SO_2 Particulate Interactions
- Atmospheric Interactions in Scrubber Plumes
- Control Technology Assessment for Energy
- Morbidity and Industrial Hygiene Study—Worker Exposure to Sulfur and Nitrogen Oxides
- Cost of Control for Precursors of Acid Deposition

for further information

publications

- Sulfur Emission: Control Technology and Waste Management. EPA Decision Series. May 1979. EPA-600/9-79-019. 33 pages.

  A nontechnical examination of sulfur emission control technology and waste management issues.

- EPA Research Outlook. February 1980. EPA-600/9-80-006. 224 pages.

  A description of EPA's plans for future environmental research.

- EPA Research Highlights. January 1980. EPA-600/9-80-005. 100 pages.

  Highlights of the EPA research and development program of 1979.

- EPA/ORD Program Guide. October 1979. EPA-600/9-79-038. 85 pages.

  A guide to the Office of Research and Development—its organizational structure, program managers, and funds available for contracts, grants, and cooperative agreements.

- Energy/Environment IV. Proceedings of the Fourth National Conference of the Interagency Energy/Environment, Research and Development Program. October 1979. EPA-600/9-79-040. 330 pages.

  The proceedings of an annual conference discussing energy/environment issues, sponsored by the Federal Interagency Energy/Environment Research and Development Program.

- Who's Who V in the Interagency Energy/Environment R&D Program. January 1980. EPA-600/9-79-017. 72 pages.

- Sulfur Oxides Control in Japan. EPA Decision Series. November 1979. EPA-600/9-79-043. 24 pages.

- Coal Cleaning with Scrubbing for Sulfur Control: An Engineering/Economic Summary. EPA Decision Series. August 1977. EPA-600/9-77-017. 16 pages.

other research summaries

- EPA Research Summary: Industrial Wastewater. June 1980. EPA-600/8-80-026. 32 pages.
- EPA Research Summary: Chesapeake Bay. May 1980. EPA-600/8-80-019. 32 pages.
- EPA Research Summary: Controlling Hazardous Wastes. May 1980. EPA-600/8-80-017. 24 Pages.
- EPA Research Summary: Controlling Nitrogen Oxides. February 1980. EPA-600/8-80-004. 24 pages.
- EPA Research Summary: Acid Rain. October 1979. EPA-600/8-79-028. 24 pages.
- EPA Research Summary: Oil Spills. February 1979. EPA-600/8-79-007. 16 pages.
- Information on the availability of these publications may be obtained by writing to:

  Publications
  Center for Environmental Research Information
  US EPA
  Cincinnati, OH 45268

technical reports and manuals

- EPA Utility FGD Survey: October - December 1979. January 1980. EPA-600/7-80-029a. (PB 80-176811, $27.00)
- Survey of Dry SO_2 Control Systems. February 1980. EPA-600/7-80-030 (PB 80-166853, $9.00)
- Field Tests of Industrial Stoker Coal-Fired Boilers for Emissions Control and Efficiency Improvement. March 1980. EPA-600/7-80-065a. (PB 80-183023, $9.00)
- Environmental Considerations of Energy-Conserving Industrial Process Changes. Executive Briefing: EPA-625/9-77-001. 25 pages. (PB 264 216, $7.50)
- Methods Development for Assessing Air Pollution Control Benefits. Volume V, Executive Summary: February 1979. EPA-600/5-79-001e. 22 pages. (PB 293 619, $4.50)
- Review of New Source Performance Standards for Coal-Fired Utility Boilers. Volume II, Economic and Financial Impacts. EPA-600/7-78-155b. 165 pages. (PB 285 855, $9.00)

- Sammis Generating Station: Meeting SO_2 and Particulate Standards with Cleaned Ohio Coals. EPA-600/7-80-009. January 1980. (PB 80-147077, $9.00)

EPA Technical Reports may be obtained by writing to:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161

or by calling (703) 557-4650

conferences and workshops

The Office of Research and Development periodically sponsors various conferences, workshops and seminars to inform environmental scientists, engineers, policymakers, and the interested public of the latest research and development accomplishments. Individuals interested in information about upcoming conferences should write to:

ORD Conference Coordinator
Center for Environmental Research Information
US EPA
Cincinnati, OH 45268

questions or comments

The Office of Research and Development invites you to address any questions or comments regarding the EPA sulfur oxide control research program to the appropriate individuals listed below:

Topic	Contacts
Fuel Cleaning	James Kilgroe Industrial Environmental Research Laboratory, MD-61 Research Triangle Park, NC 27711
Fuel Gas Desulfurization & Coal-Limestone Combustion	Robert Statnick Office of Research & Development, RD-681 US EPA Washington, DC 20460
Coal Liquefaction and Gasification	Morris Altschuler Office of Research & Development, RD-681 US EPA Washington, DC 20460

EPA's sulfur oxides control research program is administered by Dr. Steven Reznek, Deputy Assistant Administrator for Environmental Engineering and Technology.